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HPC

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EVALUATION OF HEAT
PRODUCTION FROM LIGHT
WATER ELECTROLYSIS
CELLS OF HYDROCATALYSIS
POWER CORPORATION

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Technology Development

February 25, 1994

ORIGINAL

"DRAFT"

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ABSTRACT

An experimental study was undertaken to evaluate heat production in electrolysis cells designed and set up by Hydrocatalysis Power Corporation (HPC). Results show 50% more heat production in cells with an "active electrolyte" of 0.57 molar K_2CO_3 , compared to a cell with a control electrolyte of 0.57 molar Na_2CO_3 . Other calorimetric data are presented. Evidence for the mechanism proposed by HPC is discussed, along with an alternative mechanism proposed by Arnold Isenberg. Critical experiments to resolve the question of heat production are proposed.

1. Introduction

Hydrocatalysis Power Corporation (HPC) has developed electrolysis cells that are reported to produce excess power, as heat, during electrolysis of a potassium carbonate electrolyte with a nickel cathode. This may be loosely associated with "Cold Fusion" although HPC claims an advanced quantum theory that provides a purely chemical explanation for the heat production. The effect occurs in cells containing only normal water, arguing against any nuclear phenomenon. An investigation of this heat production was undertaken to determine if there is an effect that could be the basis of advanced power generation, or if the claimed effects can be attributed to poor calorimetry or other experimental artifacts.

Following an exchange of information about requirements and facilities, Mr. William Good, of HPC, came to STC on December 7, 1993 to set up four cells for our evaluation. Experiments were conducted until December 23. This letter report is a brief summary of experiments conducted and their results.

2. Conclusions

1. Electrolysis cells provided by Hydrocatalysis Power Corporation demonstrated 50% excess heat with K_2CO_3 electrolyte, compared to a control cell containing Na_2CO_3 electrolyte.
2. Comparison of heating due to resistance of electrolysis current to heating from an immersed auxiliary heater was consistent, in some instances, with the excess heat observed with electrolyte comparison. However, design problems with the HPC cell make power balance comparisons uncertain. The design problems include the high operating temperature of the cells, and the variation of operating temperature with operating conditions.
3. Evidence for the mechanism leading to the observed anomalous heat is sparse. Data provided by HPC were unconvincing when reviewed by STC experts. In an independent experiment, Arnold Isenberg demonstrated an alternative, chemical mechanism that would not provide a basis for power production.
4. A basis for improved cell design and more significant experimental characterization of the HPC thermal effects was established by these experiments. Critical experiments were identified.

3. Recommendations

1. It is essential to determine if the anomalous heat observed in the HPC cells was due to the difference in Faraday efficiency of electrolytic gas generation between the K_2CO_3 and Na_2CO_3 electrolytes, as Isenberg observed with a different cell geometry. If the anomalous heat is only due to difference in Faraday efficiency, there is no effect worth further investigation.
2. If the heat anomaly survives the determination of Faraday efficiency, further studies should be directed at determination of scaling effects. Improved cell design features have been identified for such studies. These are described in the discussion.
3. HPC has developed a gas phase cell that does not require an electrolyte or electrolysis. These cells merit further attention.

4. Experimental:

4.1 HIGH TEMPERATURE CELLS

Initially, three cells were set up identically in 2 liter dewars. Each had a cathode made up of 500 m of 0.38 mm diameter Ni wire (ALFA, .99999 pure), giving 0.6 M^2 surface area. The cathodes were wound loosely on porous teflon forms. The anode of each cell was Pt deposited on a Ti mesh, approximately 14 cm long by 4 cm wide, folded back on itself about 6 cm. Two such pieces were used for each cell, for an approximate area of 200 cm^2 .

The cells were constructed by placing the cathode in the dewar, placing the anode down the center of the teflon form, and also placing an auxiliary heater and a thermocouple in a glass tube down the center of the teflon form. All three cells were connected in series with a common power supply. This was to ensure that equal electrolysis was done in each cell.

The components of each electrolysis cell were prepared by following a protocol established by HPC, appendix 1. Each of these first three cells was set up by Bill Good.

The cells were polarized and electrolyte, $0.57 \text{ M K}_2\text{CO}_3$, was added to permit electrolysis current to flow. This step was done as quickly as possible to ensure that no cathode was exposed to the highly basic, corrosive electrolyte without undergoing electrolysis, for more than the minimum time necessary. Initially, 1.5 l of electrolyte was added to each cell, to bring the electrolyte level to the top of the electrode assembly. Later, after the electrolyte had heated up and expanded, it was necessary to remove 100 ml of solution, leaving a charge of 1.4 l of electrolyte in each cell. The power supply was adjusted to provide a nominal electrolysis current of 3 amperes. This initial set up was somewhat rushed because Bill Good had only 3 days available at STC.

A plastic foam lid was made for each cell. The lids had some thermal insulation value, but were definitely not gas tight. Lead wires penetrated for the electrodes and for the auxiliary heater. Additional penetrations permitted insertion of the thermocouple and a small funnel that allowed for addition of water to compensate for the water lost to electrolysis, calculated to be 25 ml/day for electrolysis at 3 A.

A data collection system was set up, based on a Molytek data recorder acquired for this purpose. It was set up to measure the following parameters:

Series current

Room Temperature (measured in a dummy dewar cell containing distilled water).

For each cell:

Voltage drop

Cell temperature

Heater voltage

Heater current, measured as voltage drop across a 0.01 ohm, 1% precision resistor.

The Molytek allows channels to be used for calculations based on the information in other channels. So, for instance, the heater power was calculated for each cell. By the time the fourth cell was on line, all 32 channels of the data logger were in use.

Initial experiments were performed with 0.57 M K_2CO_3 in all 3 cells. They were run at 3 A until they reached thermal equilibrium. At those equilibrated conditions the three cells were at the following temperatures: Cell A, 68.1 °C; Cell B, 68.8 °C; and Cell C, 69.4 °C. Since the room temperature was 23.7 °C, that meant the three cells were showing very similar response, about 45 °C above ambient temperature.

The power being delivered to each cell was determined by measuring the voltage drop across each cell. The total power is then the product $I_{series} V_{cell}$ into each cell, but the power available for heating the cell is less due to the loss of heat from evolution of electrolysis gases. HPC assumes 100% Faraday efficiency for electrolysis gas evolution, so the power available for cell heating is reduced by the enthalpy of formation of the gases from water, which corresponds to 1.48 volts. Then the heating power into the cell, assuming 100% Faraday efficiency of gas formation, is

$$W_{et} = I_{series}(V_{cell} - 1.48)$$

Auxiliary heaters were placed in each cell, to permit "on-the-fly" calibration of the power balance in the cells at conditions close to any given set of operating conditions. A series of experiments were performed in which combinations of electrolysis power and heater power were applied, and the equilibrium temperatures of the cells determined. These experiments are summarized in figures 1 to 3, which show the conditions of operation summarized as the

electrolysis heating power, W_{el} , auxiliary heater power, W_{htr} , $W_{total} = W_{el} + W_{htr}$, and the heating coefficient for those conditions. Figures 4 to 6 show the temperature rise for each cell at the same conditions.

On December 20, cell A was switched from the K_2CO_3 electrolyte to Na_2CO_3 to provide a control experiment. Na_2CO_3 is not expected to be catalytic for extracting energy from H atoms, and HPC routinely use it as a control. Prior to the electrolyte switch, all three cells were again equilibrated at 3 A electrolysis current with no auxiliary heat, and were still showing similar behavior with temperatures ranging from 66.4 to 73.8 °C. After the electrolyte switch, Cell A equilibrated at 49.9 °C, while Cells B and C were at 69.2 and 74.9 °C.

4.2 LOW TEMPERATURE CELL

The high operating temperatures of the first three cells caused several problems, such as

- At such high temperature, the vapor pressure of water is approximately 0.5 atm, and the variation with temperature is significant. The gases lost through electrolysis will thus carry off an approximately equal volume of water vapor, and this loss is temperature dependent. This makes it difficult to interpret thermal effects associated with changes in power to the cell which result in operation at various temperatures.
- The resistance of the electrolyte to current flow is temperature dependent. When the heat loss coefficient of a cell is as low as that for these dewar cells, resulting in a heating coefficient of $>10^\circ C/watt$, each change in cell conditions produces a different heating effect due to operation at a different temperature.
- Water was added to each cell periodically to make up for the gases lost through electrolysis. However, the additional loss due to evaporation was significant and more difficult to compensate. When this effect became evident, one cell (B) was put on a balance to provide daily weight information. However, since this effect is temperature dependent, the same correction did not apply to all cells. Furthermore, periodic addition of cold water is equivalent to a power loss that is not considered in the power balance calculation. Adding the same amount of water to each cell balanced the

power effect, but did not adequately compensate to maintain constant electrolyte composition.

- Because of the high cell temperature, addition of auxiliary heat required the heater to run at even higher temperature. Heat conduction through the lead wires was probably significant, reducing heat into the solution and causing the heating coefficient for auxiliary heat to be low.

A fourth cell was set up, using another set of electrodes provided by HPC. Instead of a dewar, the cell was made with a 2 gallon high density polyethylene pail with a tight fitting lid. The cell setup was essentially the same as the three smaller volume dewar cells, except that the pail had enough room on the bottom to use a magnetic stirrer off to one side to provide additional stirring to supplement the mixing due to bubbles from the electrolysis. A larger (but unfiltered) power supply permitted running this cell at a higher current, up to 7 amps. This cell was filled with 7 liters of 0.57 M K_2CO_3 . Initial heating with only the auxiliary heater, at power up to 6.1 W heated this cell up to only about 1° C above ambient. When electrolysis was begun, it was set at 7 amps, with a voltage drop across the cell of 4.2 volts, giving net electrolysis heat of about 19 W. The cell equilibrated at about 32° C, 9.5° C above ambient, giving a heating coefficient of 0.5 deg/W. An attempt was made to reduce the electrolysis power to 10 W and replace that power with auxiliary heat, but under these conditions the daily variation in room temperature was larger than any other observed effect.

4.3 Results

4.3.1 Experiments with K_2CO_3 electrolyte

Initial results showed approximately 11-13 degrees/watt of heating when the cells were run with only electrolysis. When the auxiliary heaters were used in addition to the electrolysis heat, the additional heat rise was equivalent to about 8 deg/watt. Thus, the "excess heat" from electrolysis seemed to be about 50%, based on the assumption of 100% Faraday efficiency of electrolytic gas production. Other tests were designed to further check this initial observation. These consisted of various settings of electrolysis and auxiliary heater powers, illustrated by figures 1 to 3, which show the various power

levels and the observed heating coefficients for cells A, B, and C, respectively. Figures 4 to 6 show the same power data, along with the observed temperature rise for these cells. In all these figures, each point represents equilibrated behavior at the indicated conditions, based on at least several hours of stable traces observed on the chart recording of the data logger. In most cases, multiple points were recorded and plotted at constant conditions, to illustrate the reproducibility and stability of the experiments.

In figure 1, the heating coefficient for cell A is shown for electrolysis at 3 amps, with three levels of auxiliary heating of 0, 0.54 and 1.2 W. Each time the heater power is increased, the heating coefficient decreases. However, as figure 4 shows, the temperature of the cell does increase as the power is increased. Some more subtle effects are also apparent. The electrolysis power decreases a little each time the auxiliary heat is increased. This is because the conductivity of the electrolyte increases with temperature, so at constant current the voltage drops and the power decreases slightly.

Following the experiments at 1.2 W of auxiliary heat, an attempt was made to provide the same total power with electrolysis alone. The heating coefficient did increase a little, as would be expected if there is an anomalous heat source associated with electrolysis. However, as mentioned above, loss of heat from the heater through the electrical leads would also cause the same effect.

Finally, the electrolysis current was set at 3 amps again to establish the equilibrium behavior before changing the electrolyte in cell A to Na_2CO_3 . The temperature rise and heating coefficient were very close to those observed in the initial 3 A electrolysis with no auxiliary heating.

Cells B and C showed effects similar to those observed for cell A, except that their auxiliary heater levels were set at other values to get more information on the effects of auxiliary heat. However, cell C consistently had the highest temperature of the three cells, and thus was susceptible to the largest loss of water from evaporation. This became apparent when the temperature was observed to continue a slow increase under steady operating conditions, illustrated by data from Dec. 14 and 15 in figure 6. Cell resistance kept dropping and the temperature kept rising as the salt concentration increased.

25 ml of water was being added daily to each cell to replace the calculated loss due to electrolysis. However, it became clear that this was inadequate due to the likely

evaporative loss. A high capacity balance was then obtained and placed under cell B (chosen because it was intermediate in temperature). The weight change over 24 hours was about 50 g, consistent with the expectation of 25 g for electrolysis and an equal amount of evaporation if the vapor pressure of water is 0.5 atm. Accordingly, the daily water addition was changed to 50 ml per cell. This would still be expected to slightly overcompensate in cell A, the coolest cell, and undercompensate in cell C, the hottest cell. In the end, when the cells were shut down and dismantled, the volume of electrolyte in each cell was measured. Cell C was down to 1000 ml, showing a net loss of about 400 ml of water over the duration of the experiments. Cell B contained 1300 ml of electrolyte, showing that it had been fairly well replenished once the weight change information was available. Cell A had 1350 ml, but it had been changed over to Na_2CO_3 electrolyte only a few days earlier.

The electrolyte stability was a matter of concern once the evaporative loss problem was recognized. Accordingly, samples were extracted from each cell for Total Inorganic Carbon (TIC) analysis. For these electrolytes, TIC should be a direct measurement of $\text{CO}_3^{=}$ concentration. On 12/20, the three cells showed the following values of TIC:

<u>Cell</u>	<u>TIC</u> <u>molar</u>
A	0.46
B	0.47
C	0.44

Thus there seems to be some loss or destruction of carbonate under the cell operating conditions.

4.3.2 Control Experiment with Na_2CO_3 Electrolyte

Because Cell C was more erratic than the other two, and because Cells A and B were very similar, it was decided to change the electrolyte in cell A to 0.57 molar Na_2CO_3 for a control, since Na_2CO_3 is not expected to be catalytically active for hydrogen shrinking. An objective of this test was to adjust the electrolyte concentration to match the resistance of cells A and B, and thus to run them at the same input power. Since the concentration of $\text{CO}_3^{=}$ had changed,

according to the TIC measurement, the resistances were expected to be different. However, when the cells approached equilibrium and the resistance stopped changing with temperature, they turned out to be very close, so no adjustment was needed. This meant that the cells were running with nearly identical electrical input power, 3.42 W for Cell A and 3.79 W for Cell B. With a heating coefficient of 12 deg/W, one would expect cell A to be about 5 degrees cooler than cell B under these conditions. However, the equilibrated cell temperatures were A: 50° C, and B: 69° C. Cell C was at 75° C. Thus it seems that there is anomalous heat in cell B that causes >15° additional heating. If cell A is a true control, and its temperature represents the effect of resistance heating, then the true heat coefficient is about 8 deg/W, and the anomalous heat in cell B is about 50% greater. The effect of switching electrolytes is illustrated in figure 7.

Considering that the time for these experiments allowed only a few characterization tests, and no real optimization, the 50% excess heat with K_2CO_3 compared to Na_2CO_3 electrolyte seems to be the effect predicted by HPC. The actual temperature difference of 15° C is large enough to give confidence that trivial measurement errors are not the cause of the effect. However, two additional sources of information have added doubt about the HPC mechanism and to the question of whether such cells represent a source of useful heat.

4.3.3 Isenberg's Check of Faraday Efficiency

Arnold Isenberg was an interested and very helpful observer of these experiments. When I had the opportunity to describe the final results, especially the difference between the K_2CO_3 and Na_2CO_3 electrolytes, he raised a potential alternative mechanism based on the formation of percarbonates due to the reaction of dissolved oxygen with the carbonate in the electrolyte. He requested, and received, permission to conduct a brief experiment experiment, described in attachment 2, to see if this might indeed cause the observed difference in temperature rise for the two electrolytes. As he describes, the Faraday efficiency of electrolysis gas evolution in the two electrolytes was different, and the presence of peroxy species was demonstrated.

4.3.4 Byers' Review of ESCA Data

HPC has conducted a search for the "shrunk hydrogen" product of the electrode reaction that produces excess energy in these reactions. If the existence of shrunk hydrogen, at the energy levels of the Mills theory, could be proven, a promising new energy source could be assured and further development would be clearly warranted. Unfortunately, Art Byers'

evaluation of the Electron Spectroscopy for Chemical Analysis (ESCA) data presented by HPC is that the evidence is not convincing (see attachment 3).

4.3.5 Other Factors for Consideration

As will be discussed below, the cells presented for evaluation by HPC performed as expected, showing excess energy when K_2CO_3 was used for the electrolyte, compared to a control cell filled with Na_2CO_3 electrolyte. However, the time available did not allow for much parametric investigation. The data represent certain experimental conditions, but no optimization studies were performed.

Other factors should be examined before final decisions are made about this technology. In particular, the following seem worthy of consideration:

- HPC claims observation of cells that produce more heat than the total input electrolysis power. If such claims can be substantiated, alternative mechanisms involving chemicals such as percarbonates would not explain the observations.
- After a discussion of cathode preparation between Bill Good and John Jackovitz, John provided a sample of Ni felt, annealed under hydrogen at 1100°C. Initial response from HPC was that with this cathode material, a cell drawing 80 amp, with voltage drop of 2.2V, for total electric power input of 0.176W, produced 0.250W of heat. They requested 7 additional sheets of the Ni felt, to produce a cell that would develop 120W of excess heat. The effect of this cathode material could be evaluated at STC. The results of HPC tests are not known at this time.
- HPC has also described energy production in cells that use gaseous hydrogen, and which do not involve electrolysis. In these cells, high pressure H_2 is applied to a cell prepared with a coating of the catalytic K_2CO_3 , and high rates of heat production are observed. In fact, it is reported that excess energy production continues after input energy is terminated, for significant periods of time.

5. Discussion

In general, the cells provided by HPC performed as they were expected to. The heat generated by resistance to electrolysis current, assuming 100% Faraday efficiency of electrolysis gas generation, was greater than the heat generated by the pure resistance heating of the auxiliary heaters. Furthermore, the heat production was greater with K_2CO_3 than with Na_2CO_3 electrolyte, by about 50%. On the basis of these results, HPC feels that this demonstration was successful.

Unfortunately, several factors reduce one's confidence that these cells have identified an attractive heat source that could be developed for power generation purposes. These will be discussed below.

The first factor to be considered in discussion of these experiments is problems with the heat measurements. Part of the problem was that these cells operated at quite a high temperature; higher than was anticipated. The operating temperature was difficult to predict because the heat loss coefficient for this size and design of cell was unknown. When these cells turned out to equilibrate around 70° C., it caused at least three problems:

- At this temperature, the vapor pressure of water is about 0.5 atm, and it varies significantly with temperature. Thus, changing operating conditions in a way that changed temperature changed the heat loss due to evaporation of water. Furthermore, there was uncertainty about how much water to add to a cell each day for replacement of water loss due to electrolysis.
- The effect of the auxiliary heaters was difficult to interpret. The heater had to get quite hot to generate significant heating at the cell conditions. Power loss through the heater wires could be significant, and difficult to estimate. This could explain the low heating coefficient for the auxiliary heaters relative to the heating due to electrolysis.
- Finally, there was loss of inorganic carbon during the experiments, perhaps from thermal breakdown of carbonate ion, or perhaps due to aerosol formation and transport. This is evidence for chemical reactions that are not accounted for in the HPC model; how the power balances of the cells are affected is unknown.

Another feature of the heat effects was that the heating coefficient decreased any time a change was made that increased the cell temperature. This includes changes such as increasing the electrolysis current, as well as changes such as adding auxiliary heating at constant electrolysis current. This effect is probably due to increased evaporation loss, but it makes interpretation of the heat measurements more difficult.

An attempt was made to minimize the effect of temperature change by operating the cells at the same total input power by varying both heater and electrolysis powers. The equilibrated results are shown in the figures for data of 12/18 to 12/19. These results are not very conclusive; the cell temperature and heating coefficient are determined mostly by the total input power, and not on how the power is partitioned between electrolysis current and auxiliary heater. This was also the case when the same thing was tried with cell D, operating at much lower temperature.

If the temperature measurements do not show a clear heating anomaly, the effect of changing electrolyte from K_2CO_3 to Na_2CO_3 was remarkable. The intent was to change electrolyte in one cell, and to match the power input for the two cells (A and B) connected in series. This worked out quite well, and the Na_2CO_3 cell equilibrated at a temperature $20^\circ C$ lower than the cell containing the K_2CO_3 electrolyte. At first, this looked like clear confirmation of the HPC effect.

Isenberg's measurement of the difference of Faraday efficiency for the two electrolytes raises quite a different possibility for the difference in temperature between the K and Na electrolytes. He observed Faraday efficiency of 57% for K_2CO_3 in the temperature range of $55-65^\circ C$, and 69% for Na_2CO_3 at $50-55^\circ C$. This 12% difference, scaled to the 3A electrolysis current, would account for about half of the observed temperature anomaly. Given the difference in geometries of the experiments, it is not clear how to compare them. Isenberg's setup had the anode and cathode concentric with a thin insulator between them, giving maximum opportunity for the recombination reaction. In the cells described in this report, the electrode separation was much greater, but there was sufficient agitation of the electrolyte solution that when the cells were opened on 12/23, the electrolyte was very uniformly filled with tiny bubbles. This was good in terms of providing sufficient agitation to provide uniform temperature in the cell, but possibly also of promoting recombination.

In contrast to Isenberg's experiment, the daily weight loss in Cell B indicated loss of 50 g of water/day. This is fully consistent with 100% Faraday efficiency plus loss of an equal



amount of water due to evaporation at the 0.5 atm vapor pressure of water at the cell temperature. Alternatively, the 50 g/day loss could result from lower Faraday efficiency and evaporative loss if there is significant formation and transport of aerosol from the cells.

5.1 Additional Studies

Some additional experiments, based on these preliminary observations, should be able to resolve the issues raised here. The following approach is suggested:

1. It is essential to determine if the depolarization observed by Isenberg, attributed to chemical reactions leading to the formation of percarbonates, caused the difference in temperature between cells when Na was substituted for K in the electrolyte. The principle change in our setup required would be to use a sealed lid on the cell with a vent for gas release, which would permit the evolved gases to be measured and characterized. Hard plastic lids that would meet this need were machined, but there was not time to use them.
2. The sealed cell configuration of test 1 would also permit examination of the effect of increased agitation to assure uniform temperature distribution in the cell, and a test of a mechanism proposed by Gene Struhl (Baltimore, retired). He has proposed that the heat observed results from chemical reaction of the hydrogen formed at the cathode, and that the effect could be enhanced by sparging with oxygen, or diminished by sparging with nitrogen. Sparging would provide a way of varying the agitation in the cell, as well as a way to investigate the effect of the sparging gas on cell heat production.

The results of these tests 1 and 2 would determine the Faraday efficiency of electrolytic gas production in our cells. If it is shown that the observed temperature anomaly is a result of differing Faraday efficiencies for the two electrolytes, there would be no reason to pursue further experiments at this time. However, it would be desirable to continue to monitor developments that might indicate true anomalous heat production, particularly in gas phase cells in which the problems associated with electrolysis do not arise.

If the observed heat anomaly survives the Faraday efficiency test, there are a number of additional tests that should be considered as a sound development program. These include the following:

- It will be very valuable to establish a mode of operation that will permit separation of the cell temperature from the cell power. This can be done by operating a flow cell in which flowing electrolyte is introduced into the cell at a preset (variable) temperature, and the temperature rise in the cell is determined. In such a flow cell, the temperature rise can be controlled by controlling the flow rate. Shorter residence time in the cell should also minimize electrolyte destruction, and permit determination of electrolyte stability. Experimental parameter variations will be under much better, controlled conditions. Jim Bauerle has considered the design of a flow calorimeter for such experiments, and his input will be invaluable in designing and carrying out these tests.
- The cooperation between John Jackovitz and Bill Good has identified Ni mesh, annealed under H_2 at $1100^\circ C$ as a cathode material with the potential to produce true excess energy greater than the product of cell voltage times current. This electrode material should be employed in our well designed flow cell.
- HPC recommends understanding electrolysis cells before trying experiments with gas cells. However, the gas cells provide a possible route to the high temperature operation needed for power generation, without the problems associated with carrying out electrolysis in aqueous solution at temperatures above the boiling point of water. An objective of advanced testing should be to test and characterize gas cells, including use of the $1100^\circ C$, H_2 annealed Ni felt as the catalytic surface.

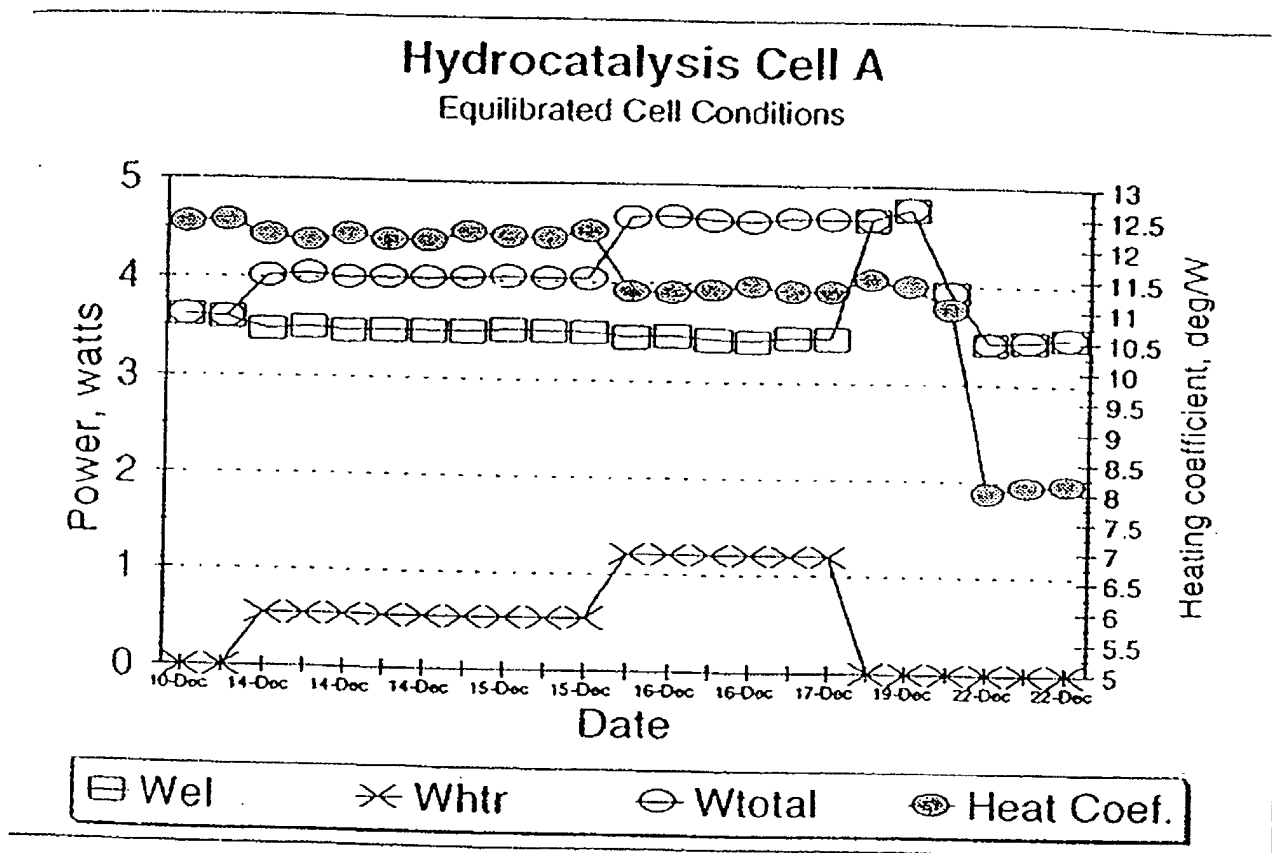


Figure 1. Equilibrated values for heating coefficient of cell A at various conditions of input power. Points before 12/22 are with K_2CO_3 electrolyte; last three points are with Na_2CO_3 electrolyte.

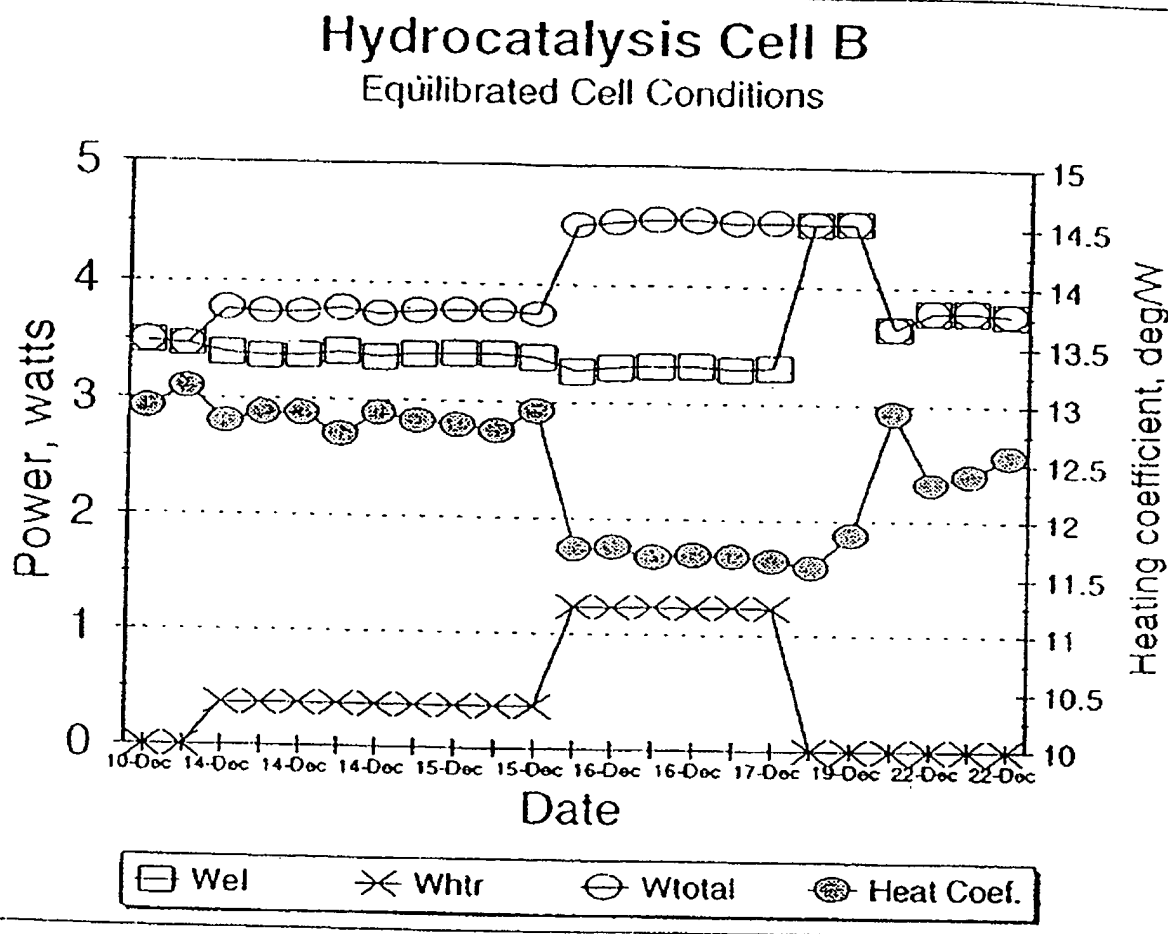


Figure 2. Equilibrated values for heating coefficient of cell B at various conditions of input power. All points are with K_2CO_3 electrolyte.

Hydrocatalysis Cell C

Equilibrated Cell Conditions

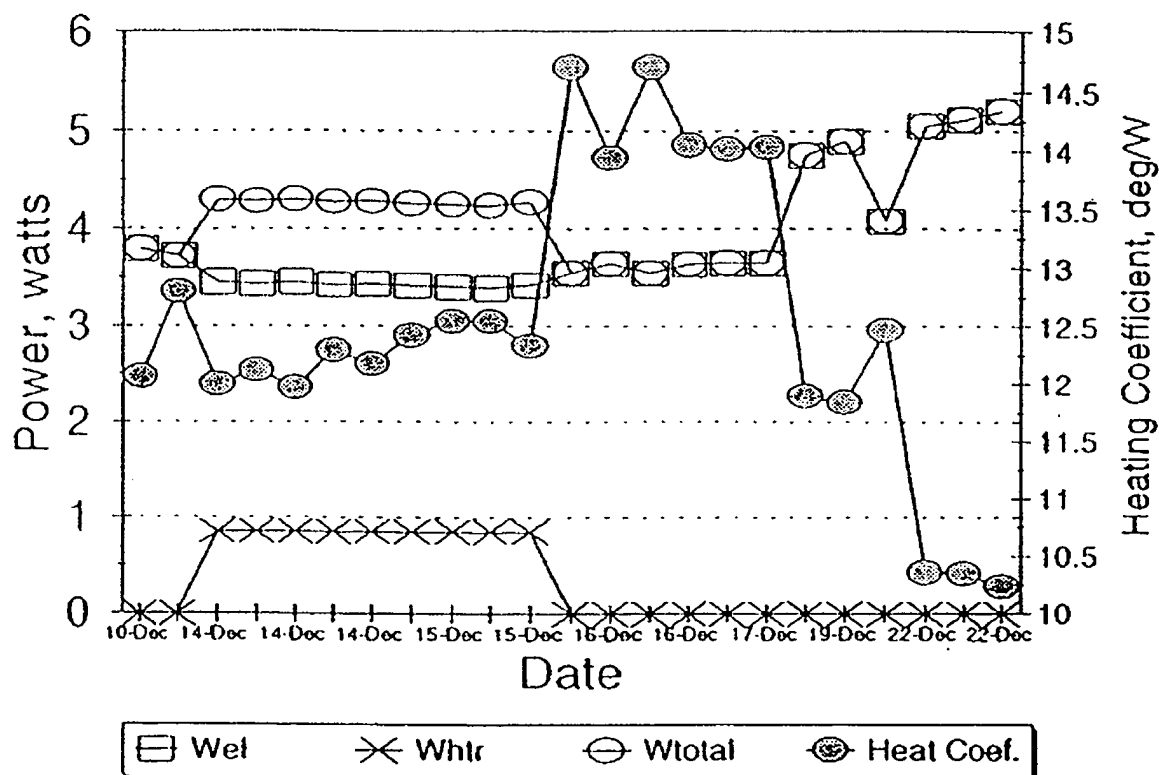


Figure 3. Equilibrated values for heating coefficient of cell C at various conditions of input power. All points are with K_2CO_3 electrolyte.

Hydrocatalysis Cell A

Temperature rise vs input power

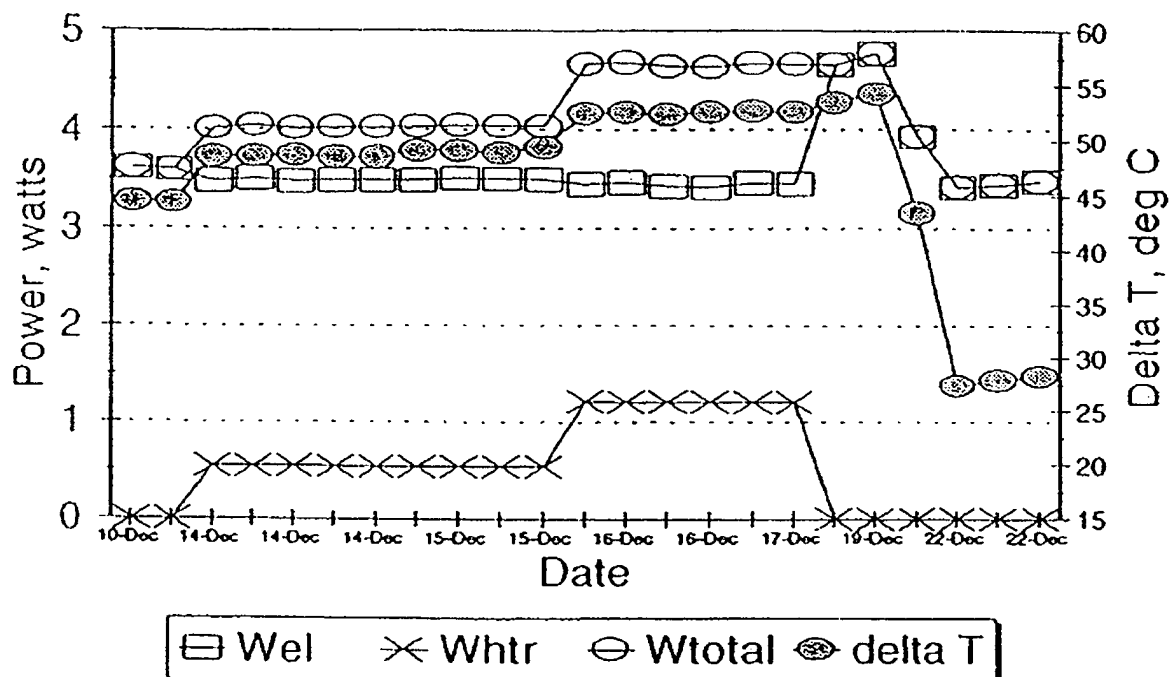


Figure 4. Equilibrated values for temperature rise (ΔT) of cell A at various conditions of input power. Points before 12/22 are with K_2CO_3 electrolyte; last three points are with Na_2CO_3 electrolyte.

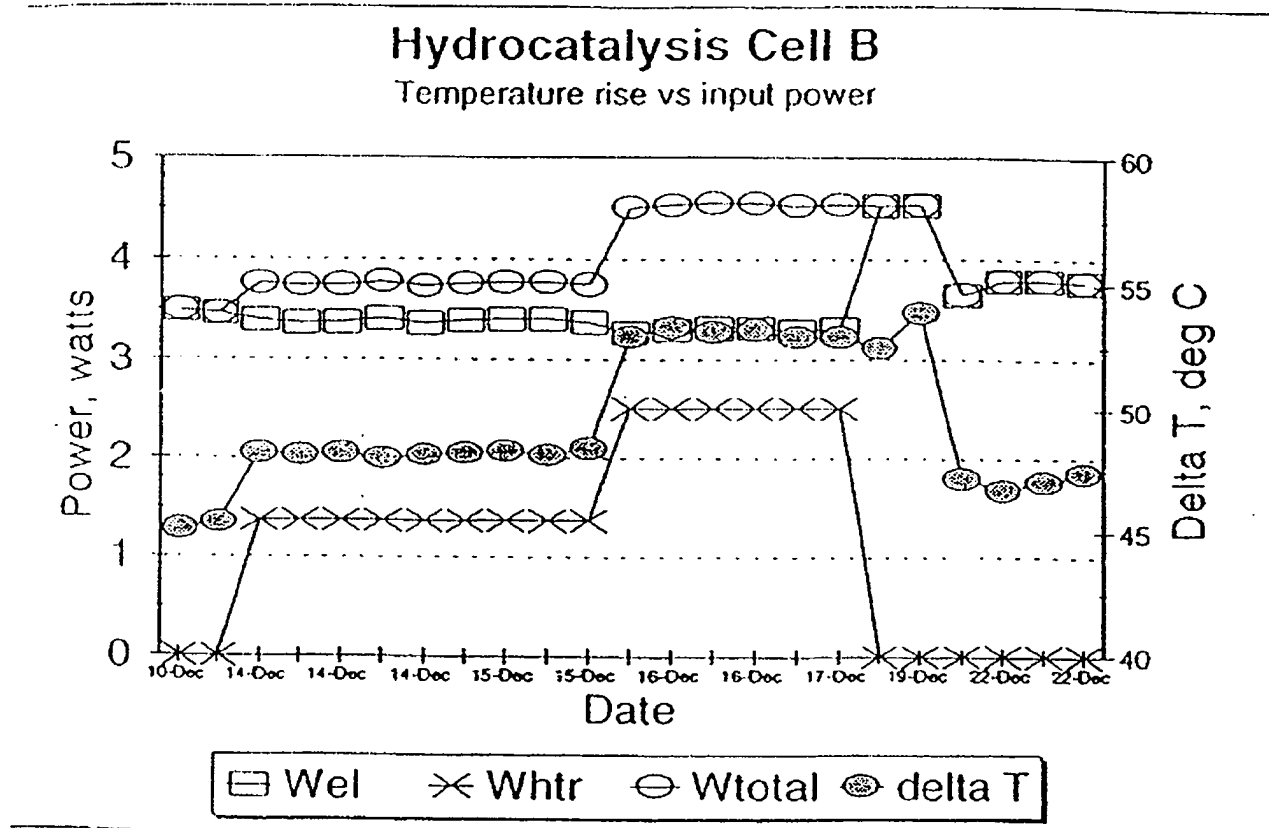


Figure 5. Equilibrated values for temperature rise (ΔT) of cell B at various conditions of input power. All points are with K_2CO_3 electrolyte.

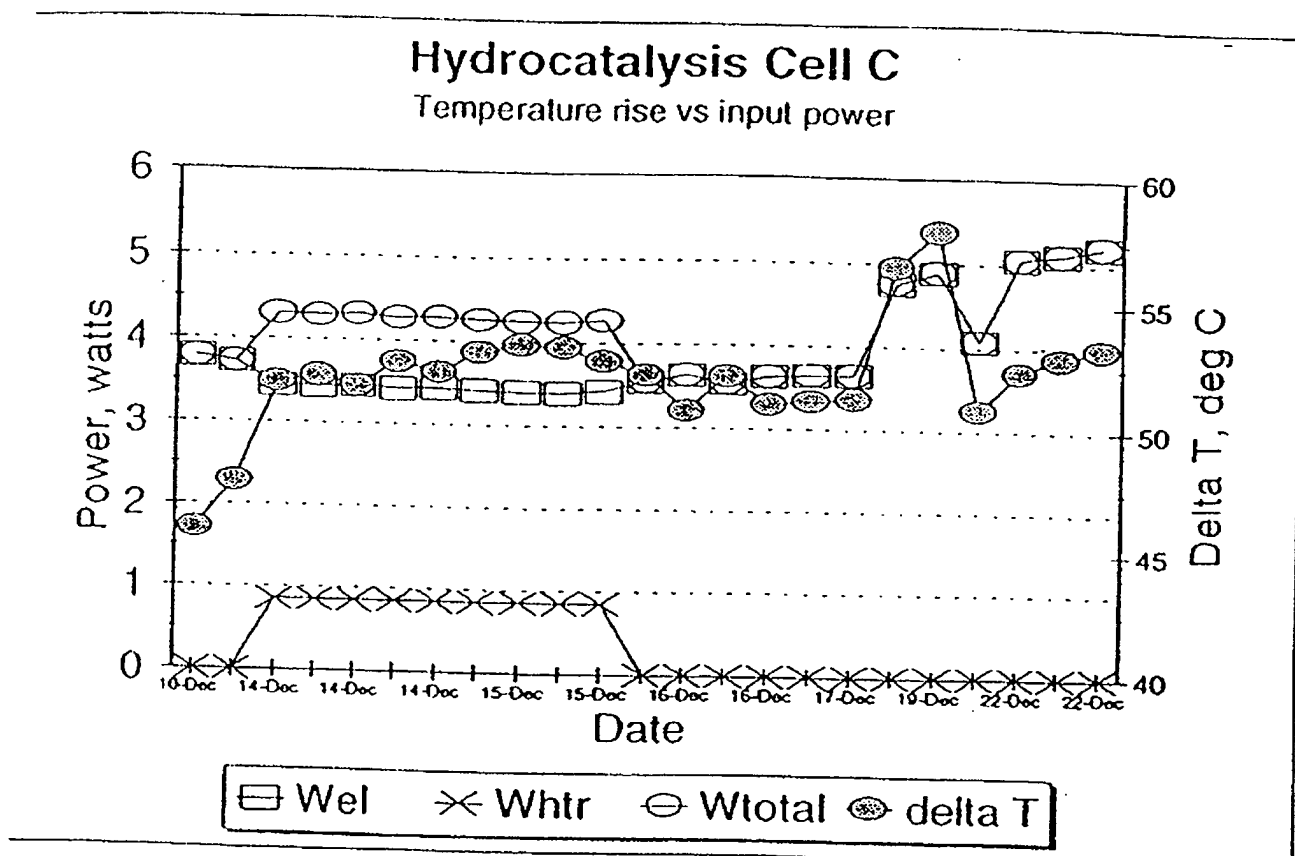


Figure 6. Equilibrated values for temperature rise (ΔT) of cell C at various conditions of input power. All points are with K_2CO_3 electrolyte.

Hydrocatalysis Data Effect of Na₂CO₃ in Cell A

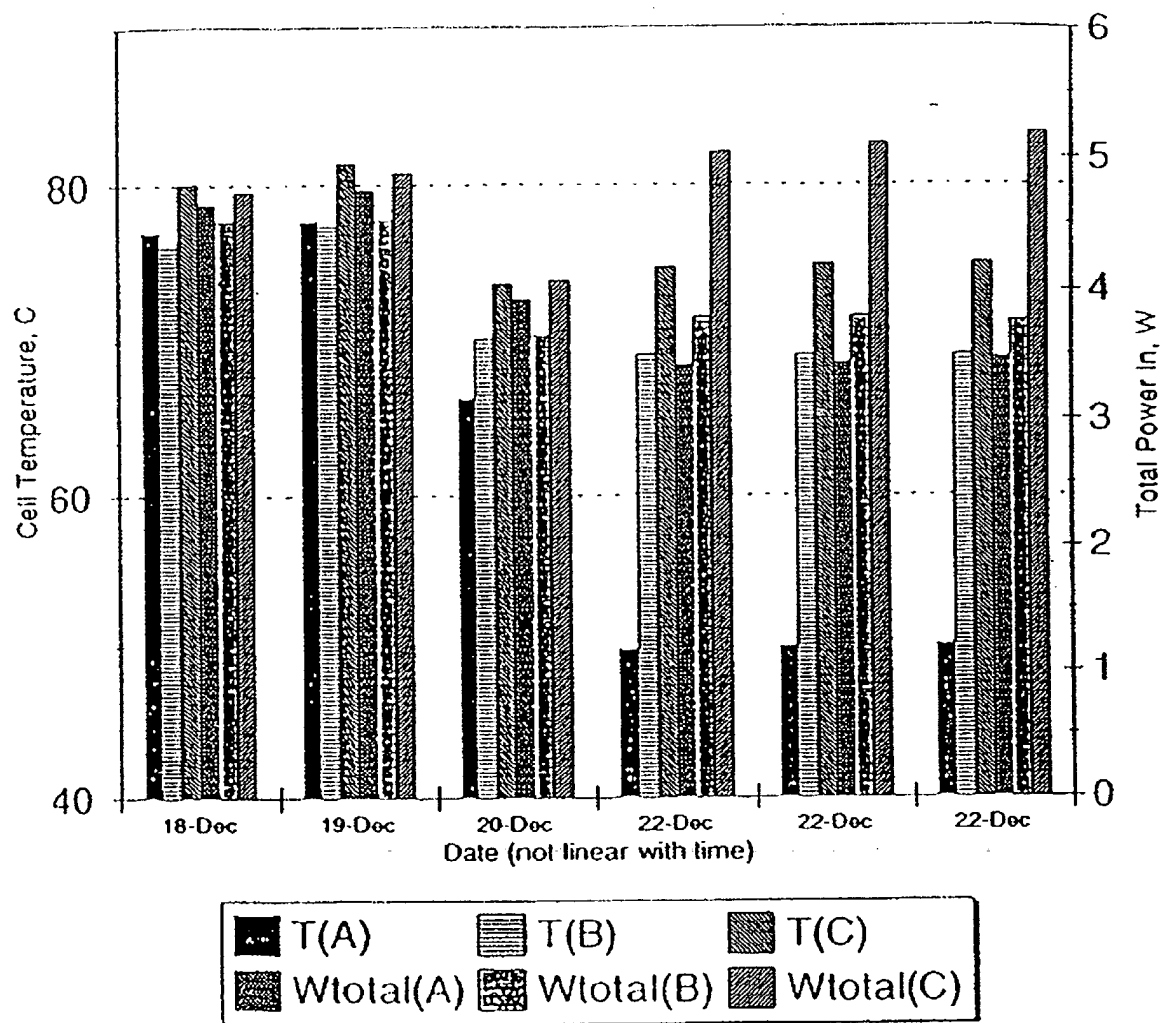


Figure 7. Effect of changing electrolyte in cell A from K₂CO₃ (before 12/22) to Na₂CO₃. Bars show equilibrated temperature for various input power conditions.

Attachment 1
HPC Experimental Protocol

Attachment 2
Isenberg's Determination of Faraday Efficiency



CS 94-002

From: Science & Technology Center
WIN: 236-2157
Date: January 14, 1994
Subject: Thermal Effects in Electrolysis of Aqueous K_2CO_3 -Solutions

To: S. H. Peterson 501-3E17
cc: W. J. Dollard 501-2W59
S. D. Harkness 801-3C54C
J. A. Spitznagel 801-3C54D
P. R. Emlage 501-2B32

Recently you conducted some nice calorimetric measurements on electrochemical cells during the electrolysis of potassium- and sodium-carbonate solutions, in order to verify data that had been obtained by R. L. Mills and W. R. Good of HydroCatalysis Power Corporation using anode/cathode hardware, that they provided to you. As you informed me, you confirmed that the thermal effects during the electrolysis of K_2CO_3 solutions were significantly more exothermic than in Na_2CO_3 solution as electrolyte.

Mills and Good have observed this effect and explained it through a rather bizarre theory involving new energy states of hydrogen. The thermal effects, in my view, needed an immediate rational explanation. Therefore, I conducted several electrochemical measurements that can explain higher exothermal reactions during the electrolysis of aqueous K_2CO_3 -solutions as compared to Na_2CO_3 -solutions. In the interpretation of enthalpy measurements as proposed by Mills and Good, the assumptions are made that the faradaic efficiency with respect to gas evolution is 100%. This assumption enters into the computation as a loss of energy from the calorimetric system. However, when electrochemical side reactions take place, gas evolution rates may be reduced and the side reactions can contribute to exothermic effects within the calorimeter. Computations, therefore, must take such thermal effects into account.

I electrolyzed aqueous solutions of K_2CO_3 and Na_2CO_3 within the confines of a 500 ml gas burette, in order to measure the total volume of gas evolving from anode and cathode. The rate of gas evolution was measured and pressure, temperature, and humidity corrections were made. No special pretreatment (purification) of electrodes or electrolyte were made. I suspected anodic side reactions could involve the formation of percarbonates (adducts of hydrogen peroxide and carbonates). These compounds would depolarize (be reduced at) the cathode and lead to a lower than theoretical rate of gas evolution (<10.45 ml gas per ampere minute).

The presence of percarbonates can be detected by acidifying the electrolyte and by subsequent reaction of the solution with potassium iodide. The presence of H_2O_2 (from percarbonate) will lead to the formation of free iodine which is colorimetrically detected with a starch indicator. Both electrolyte solutions did show a strong iodine reaction after electrolysis had been performed, thus, explaining the low efficiency in observed gas evolution.

The essential experimental data are summarized in Table 1 and the simple electrolysis apparatus is shown in Figure 1.

Following observations have been made:

- Gas evolution in both electrolytes is significantly below 100%.
- Higher efficiency of gas evolution is observed in the Na_2CO_3 -electrolyte, which explains higher enthalpy values in an otherwise "mirror" K_2CO_3 system.
- Increased electrolyte temperature decreases gas evolution efficiency in both electrolyte solutions significantly.

The last observation was not expected because H_2O_2 is less stable at higher temperature. This would indicate that the cathode depolarization reaction rate determines the gas evolution efficiency. This rate would be expected to go up with temperature.

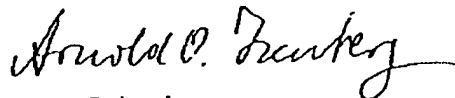
Conclusions:

- Comparison of thermal effects in the electrolysis of K_2CO_3 and Na_2CO_3 can only be made if careful gas evolution and gas composition analysis is conducted in addition to the calorimetric measurements.
- Anodic/cathodic side reactions in the two electrolysis systems are expected to depend very much on the geometry of the electrochemical cell, current density, temperature, electrolyte volume, and power supply current profiles.
- The experimental apparatus of this study underestimates gas evolution inefficiencies because of a relative low current (as compared to 3A in your calorimetric experiment), higher dilution of anodic by-products (2 liter electrolyte), and partial removal of anodic by-products from the electrolysis cell active region by the increasing gas column in the gas burette/electrolysis cell envelope.

The latter point is demonstrated by comparison of experiment 1 and 2 in Table 1. Before the start of the second experiment, the electrolyte had been enriched with anodic by-products from the first experiment. Then, the electrolyte column in the

burette was raised to the top and during the second experiment the electrodes operated in an environment of accumulated anode by-products. This explains the lower gas evolution rate under otherwise similar conditions.

Please feel free to use this information in the interpretation of your carefully executed calorimetric measurements.



Arnold O. Isenberg
Consulting Scientist
Advanced Energy Conversion Division

dk

Attachments

P.S.: One could tell the "hydrido theoreticians" to use sodium or potassium borate solutions as electrolyte. The expected anodic by-product concentrations would be even higher (perborates) and the expected "unexplainable" thermal effects would be even more exothermic (if one conveniently assumes 100% gas evolution efficiency). Sorry, there is a little bit of a nasty streak to me!

Table 1
Efficiency of Gas Evolution in
Alkaline Carbonate Electrolysis Cells

Experiment #	Electrolyte Type	Electrolyte Temperature °C	Current A	Collected Gas Volume ml, S.T.P.	Gas Evolution Rate ml/min	Gas Evolution Efficiency %
1	0.57m K_2CO_2	19	1.00	216.7.	7.01	67.1
2	0.57m K_2CO_3	19	1.00	260.9	6.74	64.5
3	0.57m Na_2CO_3	22	1.00	256.3	7.92	75.8
4	0.57m Na_2CO_3	50-55	1.00	250.3	7.18	68.8
5	0.57m K_2CO_3	55-65	1.00	252.0	5.98	57.2
6	0.57m K_2CO_3	65-70	1.00	251.5	5.89	56.4

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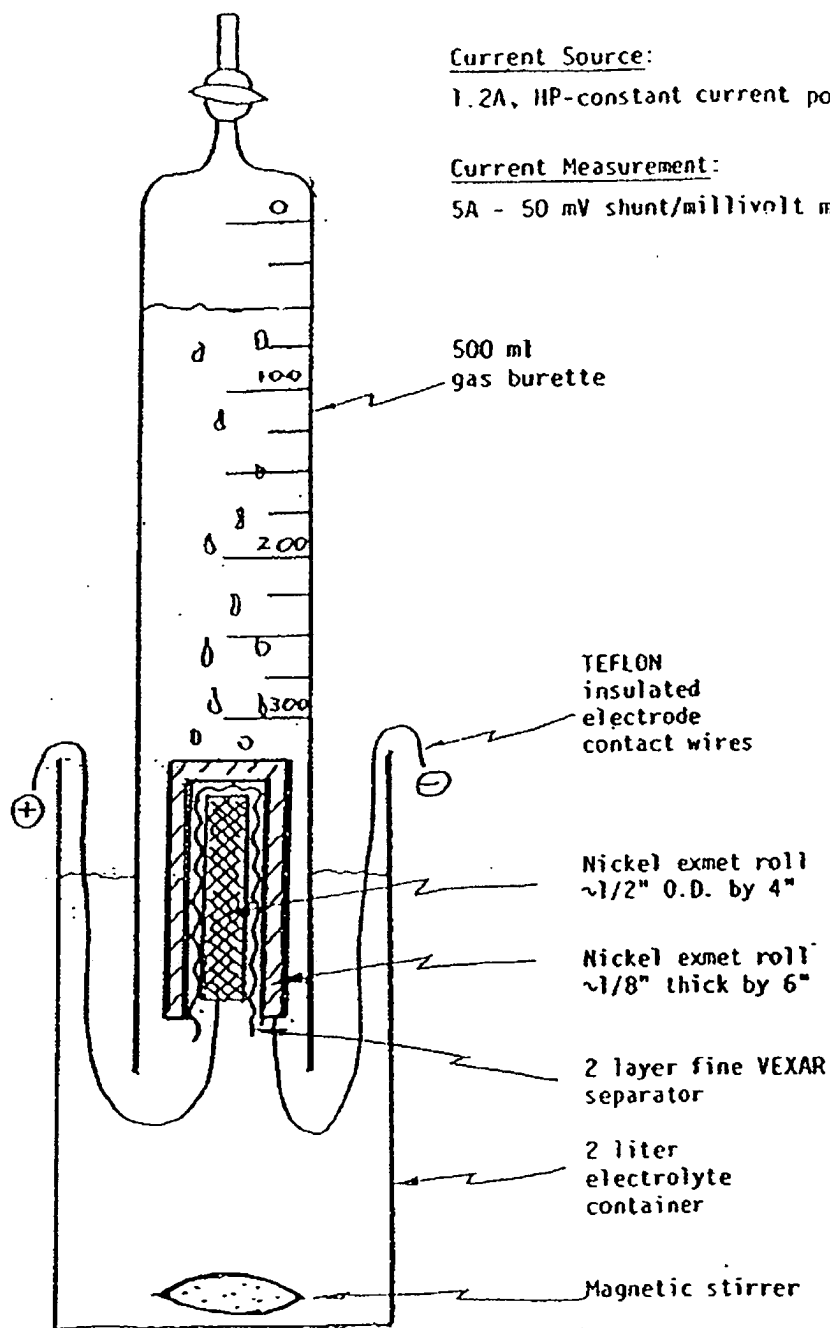


Fig. 1 - Gas meter - electrolysis cell.

Attachment 3
Byers' Review of ESCA Evidence for the
Existence of "Shrunken Hydrogen"

From: SCIENCE & TECHNOLOGY CENTER
WIN: 236-1678
Date: January 18, 1994
Subject: *Review of ESCA Evidence for Fractional Quantum Energy Levels of Hydrogen*

To: STC
John Spitznagel

cc: S. H. Peterson
A. Isenberg
R. J. Jacko
W. G. Clark, Jr.

I have reviewed the paper by Randell L. Mills and William R. Good on the evidence for fractional quantum energy levels of hydrogen. This paper proposes the creation "hydrino" atoms on nickel electrodes during the electrolysis of aqueous potassium carbonate. The proposed hydrino atoms are hydrogen atoms which have dropped into a new electronic ground state where $n=1/2$. The existence of this fractional quantum level is used to explain the production of heat in electrolysis experiments which was previously attributed to cold fusion. ESCA characterization of the nickel electrodes was used to support the hydrino theory.

The ESCA evidence consisted of a broad peak at 55 eV binding energy in a spectrum from an electrode in which excess heat was observed. This is the binding energy which was predicted for an electron in a hydrino atom. The authors state that "There is no known atom which has an electron with a binding energy in this region that was present in the electrolytic cell." While it is true that none of the elements which were intentionally added to the cell have electrons with binding energies in this area, the possibility of the presence of trace impurity elements must be considered. A cathodic electrode will concentrate even ultratrace elements to levels detectable by ESCA.

A search of the NIST XPS database identified a number of compounds which had elements with photoelectron transitions in this area. The most common are compounds of iron. The binding energy for Fe 3p electrons ranges between 52.8 and 57.95 eV depending on the oxidation state of the iron. The broad peak which was observed is common for iron compounds of mixed valence state or for iron

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oxide mixtures. The presence of iron could be confirmed by looking at the more intense 2p photoelectron peak which have a binding energy near 710 eV. The ESCA scan in the Mills paper went no higher than 310 eV. Compounds of lithium and osmium could also have produced peaks in the 55 eV region. The authors would have built a more convincing argument for a new quantum state had they addressed the impurity issue.

Another consideration which sheds doubt on the authors interpretation of the ESCA results is that the lightest elements are very difficult to detect. The minimum detection limit for lithium is typically near 10 atomic %, and hydrogen cannot be detected at all under normal conditions. The expected poor detection limit for the hydrido atom requires that it be present at high concentration at the nickel electrode surface. This is unlikely because of the high vacuum required for ESCA.

In summary, the ESCA data presented by Mills and Good does not provide strong evidence for fractional quantum states of hydrogen.

Art Byers

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